Compensation of Magnetic Impurity Effect in Superconductors by Radiation Damage

Mi-Ae Park[a,1], M. H. Lee[a], and Yong-Jihn Kim[b,*]

[a] *Department of Physics, Seoul National University, Seoul 151-742, Korea*

[b] *Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea*

Compensation of the reduction of T_c caused by magnetic impurities has been observed as a consequence of radiation damage. Using the recent theory by Kim and Overhauser (KO) we consider the effect of radiation damage on the T_c of superconductors having magnetic impurities. We find a good fitting to the experimental data. It is also pointed out that Gor'kov's formalism with the pairing constraint derived from the Anomalous Green's function leads to KO theory.

KEYWORDS: irradiation effect, magnetic impurity, BCS model

Gor'kov's formalism, pairing constraint

[1] Present address: Department of Physics Education, Seoul National University, Seoul 151-742, Korea

[*] Corresponding author. URL: http://taesan.kaist.ac.kr/~yjkim

1. INTRODUCTION

Recently Kim and Overhauser (KO)[1] obtained different results for the magnetic impurity effect on superconductors compared with those of Abrikosov and Gor'kov's theory.[2] First, the initial slope of T_c decrease by magnetic impurities is found to depend on the superconductor and therefore is not the universal constant proposed by Abrikosov and Gor'kov. Second, the reduction of T_c by magnetic impurities is significantly lessened whenever the mean free path ℓ becomes smaller than the BCS coherence length ξ_o. This compensation phenomenon has been observed by adding non-magnetic impurities[3–5] and radiation damage,[6–8] whereas prior theories predict that magnetic impurity effect is not influenced by the non-magnetic scattering.

In this paper we compare the theoretical T_c values calculated by KO theory with the data of Hofmann, Bauriedl, and Ziemann.[8] Fairly good agreement was found. Hofmann et al. irradiated pure In and In + 400 ppm Mn foils with Ar ions. A $\Delta T_c = 2.2K$ in T_c for a pure 70 nm In film compared to an identical film ion implanted with 400 ppm Mn was changed to $\Delta T_c = 0.3K$ after both films were exposed to a 275 kev Ar^+-ion fluence of $2.2 \times 10^{16} cm^{-2}$. Both films were maintained below 15K during the Ar^+ irradiation. The reason of this compensation phenomenon is that only magnetic solutes within $\xi_{eff} \sim (\ell\xi_o)^{\frac{1}{2}}$ of a Cooper pair's center of mass can diminish the pairing interaction.

We also point out the problem inherent in the self-consistency equation of the Gor'kov's formalism.[9,10] In the presence of the magnetic impurities the self-consistency equation fails to choose a correct pairing, which is consistent with the physical constraint of the system. The self-consistency equation allows some extra pairing terms forbidden by the physical constraint. The remedy is the following: we first find a correct form of the Anomalous Green's function satisfying the physical constraint and then derive a self-consistency equation from it. In that case the revised self-consistency equation gives nothing but Kim and Overhauser's result.[1]

2. BCS-TYPE THEORY BY KIM AND OVERHAUSER

We will briefly review KO's approach.[1] The magnetic interaction between a conduction electron at $\mathbf{r}$ and a magnetic impurity (having spin $\mathbf{S}$), located at $\mathbf{R}_i$, is given by

$$H_m(\mathbf{r}) = J\mathbf{s}\cdot\mathbf{S}_i v_o \delta(\mathbf{r}-\mathbf{R}_i), \tag{1}$$

where $\mathbf{s} = \frac{1}{2}\sigma$ and v_o is the atomic volume. In the presence of the magnetic impurities BCS pairing must employ degenerate partners which have the $J\mathbf{s}\cdot\mathbf{S}_i$ scattering built in because the strength of exchange scattering J is much larger than the binding energy. This scattered state representation was first introduced by Anderson in his theory of dirty superconductors.[11] The scattered basis state which carries the label, $\vec{k}\alpha$, is

$$\psi_{\vec{k}\alpha} = N_{\vec{k}}\Omega^{-\frac{1}{2}}[e^{i\vec{k}\cdot\vec{r}}\alpha + \sum_{\vec{q}} e^{i(\vec{k}+\vec{q})\cdot\vec{r}}(W_{\vec{k}\vec{q}}\beta + W'_{\vec{k}\vec{q}}\alpha)], \tag{2}$$

where,

$$W_{\vec{k}\vec{q}} = \frac{\frac{1}{2}J\overline{S}v_o\Omega^{-1}}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}}\sum_j sin\chi_j e^{i\phi_j - i\vec{q}\cdot\mathbf{R}_j} \tag{3}$$

and,

$$W'_{\vec{k}\vec{q}} = \frac{\frac{1}{2}J\overline{S}v_o\Omega^{-1}}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}}\sum_j cos\chi_j e^{-i\vec{q}\cdot\mathbf{R}_j}. \tag{4}$$

χ_j and ϕ_j are the polar and azimuthal angles of the spin $\mathbf{S}_j$ at $\mathbf{R}_j$, and the ϵ's are the electron energies of the host. The perturbed basis state for the degenerate partner of (2) is:

$$\psi_{-\vec{k}\beta} = N_{\vec{k}}\Omega^{-\frac{1}{2}}[e^{-i\vec{k}\cdot\vec{r}}\beta + \sum_{\vec{q}} e^{-i(\vec{k}+\vec{q})\cdot\vec{r}}(W^*_{\vec{k}\vec{q}}\alpha - W'^*_{\vec{k}\vec{q}}\beta)]. \tag{5}$$

At each point $\vec{r}$, the two spins of the degenerate partner become canted by the mixing of the plane wave and spherical-wavelet component. Consequently, the BCS condensate is forced to have a triplet component because of the canting caused by the exchange scattering. The new matrix element between the canted basis pairs is (to order J^2)

$$V_{\vec{k}'\vec{k}} = -V < cos\theta_{\vec{k}'}(\vec{r}) >< cos\theta_{\vec{k}}(\vec{r}) >, \tag{6}$$

where θ is the canting angle. The angular brackets indicate both a spatial and impurity average. It is given

$$< cos\theta_{\vec{k}}(\vec{r}) > \cong \ 1 - 2|W_{\vec{k}}|^2, \tag{7}$$

where $|W_{\vec{k}}|^2$ is the relative probability contained in the virtual spherical waves surrounding the magnetic solutes (compared to the plane-wave part). From Eqs. (2)-(4) we obtain

$$|W_{\vec{k}}|^2 = \frac{J^2 m^2 \bar{S}^2 c_m R}{8\pi n \hbar^4}. \tag{8}$$

Because the pair-correlation amplitude falls exponentially as $exp(-r/\pi\xi_o)$[12] at $T = 0$ and as $exp(-r/3.5\xi_o)$[13] near T_c, we set

$$R = \frac{3.5}{2}\xi_o. \tag{9}$$

Then one finds

$$< cos\theta >= 1 - \frac{3.5\xi_o}{2\ell_s}, \tag{10}$$

where $\ell_s = v_F\tau_s$ is the mean free path for exchange scattering only.

The BCS T_c equation still applies after a modification of the effective coupling constant according to Eq. (6):

$$\lambda_{eff} = \lambda < cos\theta >^2, \tag{11}$$

where the BCS λ is N_oV. Accordingly, the BCS T_c equation is now,

$$k_BT_c = 1.13\hbar\omega_D e^{-\frac{1}{\lambda_{eff}}}. \tag{12}$$

The initial slope is given

$$k_B(\Delta T_c) \cong -\frac{0.63\hbar}{\lambda\tau_s}. \tag{13}$$

The factor $1/\lambda$ shows that the initial slope depends on the superconductor and is not a universal constant. For an extended range of solute concentration, KO find

$$< cos\theta >= \frac{1}{2} + \frac{1}{2}[1 + 5(\frac{u}{2})^2]^{-1} e^{-2u}, \tag{14}$$

where

$$u \equiv 3.5\xi_{eff}/2\ell_s. \tag{15}$$

When the conduction electrons have a mean free path ℓ which is smaller than the coherence length ξ_o (for a pure superconductor), the effective coherence length is

$$\xi_{eff} \approx \sqrt{\ell\xi_o}. \tag{16}$$

For a superconductor which has ordinary impurities as well as magnetic impurities, the total mean-free path ℓ is given by

$$\frac{1}{\ell} = \frac{1}{\ell_s} + \frac{1}{\ell_o}, \tag{17}$$

where ℓ_o is the potential scattering mean free path. It is clear from Eq. (16) that the potential scattering profoundly affects the paramagnetic impurity effect. In other words, the size of the Cooper pair is reduced by the potential scattering and the reduced Cooper pair sees a smaller number of magnetic impurities. Accordingly the magnetic impurity effect is partially suppressed. This is the origin of the compensation phenomena observed in experiments.[3–8]

3. COMPARISON WITH EXPERIMENTS

Now we compare the KO theory with experiment. In Fig. 1 the T_c of In (open symbols) and InMn (closed symbols) were plotted as a function of Ar^+ fluence. The data are due to Hofmann, Bauriedl, and Ziemann.[8] Well annealed In-Films with the thickness of 70nm were prepared. The mean value of the residual resistivities, ρ_i, was $0.62\mu\Omega$ with a variation of 20%. During the irradiation, In-films were maintained below 15K. As you see, irradiation induces the increase of the transition temperature of In-film, which may be due to the

increase of electron-phonon interaction. Open symbols were fitted by the BCS T_c equation with

$$\lambda = 0.284 \times tanh(0.55\Phi + 1.76). \tag{18}$$

Φ denotes the Ar^+ fluence/10^{16}. The Debye frequency ω_D of In was set to be 129K. Closed symbols show the transition temperature of In-Mn alloys which were irradiated with Ar^+ after the Mn-implantation. 400PPM of Mn was implanted and led to $\Delta T_c \approx 2.2K$. Notice that Ar^+ irradiation not only increases the T_c as in the case of In-film but also suppress the T_c decrease caused by Mn implantation. This compensation of magnetic impurity effect by radiation damage contradicts Abrikosov-Gor'kov's theory. Merriam et al.[3] also found that adding dilute concentrations of ordinary impurities such as Pb or Sn to bulk In samples significantly reduces the magnetic impurity effect.

As we saw in Sec. 2, the ratio of the effective coherence length to the spin disorder scattering length, $\xi_{eff}/\ell_s \approx \sqrt{\ell\xi_o}/\ell_s$, determines T_c. Using the Drude formula, $\rho = m/ne^2\tau$, we can calculate the electron mean free path $\ell = v_F\tau$. For In $n = 1.15 \times 10^{23} cm^{-3}$ and $v_F = 1.74 \times 10^8 cm/sec$. The residual resistivity increase due to the Mn-implantation is estimated to be $\Delta\rho_{Mn} \approx 1\mu\Omega cm$. On the other hand, the residual resistivity increase, $\Delta\rho_{Ar}$, due to Ar irradiation, measured by by Hofmann, Ziemann, and Buckel,[14] was fitted by

$$\Delta\rho_{Ar} = 6.5ln(\Phi + 1). \tag{19}$$

Consequently, the total resistivity, ρ_{tot}, is

$$\begin{aligned} \rho_{tot} &= \rho_i + \Delta\rho_{Ar} + \Delta\rho_{Mn} \\ &= 0.62 + 6.5ln(\Phi + 1) + 1.0. \end{aligned} \tag{20}$$

From the total resistivity we can calculate ℓ and the effective coherence length. With the effective coherence length we readily find T_c by the BCS T_c equation. The theoretical curve shown (lower solid curve) involves just one adjustable parameter, τ_s, in order that $T_{co} = 1.15K$, the observed value without irradiation. We used $\ell_s = 35330\mathring{A}$. Because the

In films are actually quasi-two dimensional, there may be some corrections due to the finite thickness, which seem to be negligible in dirty limit. Nevertheless the agreement is fairly good considering some uncertainties in the film thickness effect and in the calculation of the total resistivity.

4. GOR'KOV'S FORMALISM WITH PAIRING CONSTRAINT

This compensation phenomenon contradicts prior theories for magnetic solutes.[2] The failure of Abrikosov and Gor'kov's theory originates from the inclusion of the *extra pairing* terms which violate the physical constraint of the Anomalous Green's function $F(\mathbf{r},\mathbf{r}')$.[9,10,15] Now we show how we can obtain the result of KO theory from the Gor'kov's formalism. For simplicity let's consider only the (spin-nonflip) z-component of the magnetic interaction. Gor'kov's self-consistency equation is given

$$\Delta(\mathbf{r}) = VT\sum_{\omega}\int \Delta(\mathbf{l})G^{\uparrow}_{\omega}(\mathbf{r},\mathbf{l})G^{\downarrow}_{-\omega}(\mathbf{r},\mathbf{l})d\mathbf{l}, \tag{21}$$

where

$$G^{\uparrow}_{\omega}(\mathbf{r},\mathbf{l}) = \sum_{\vec{k}} \frac{\psi_{\vec{k}\uparrow}(\mathbf{r})\psi^{*}_{\vec{k}\uparrow}(\mathbf{l})}{i\omega - \epsilon_{\vec{k}}}, \tag{22}$$

and

$$G^{\downarrow}_{-\omega}(\mathbf{r}',\mathbf{l}) = \sum_{\vec{k}'} \frac{\psi_{\vec{k}'\downarrow}(\mathbf{r}')\psi^{*}_{\vec{k}'\downarrow}(\mathbf{l})}{-i\omega - \epsilon_{\vec{k}'}}. \tag{23}$$

Note that $\psi_{\vec{k}\uparrow}$ denotes only the spin-up component of the wavefunction Eq. (2) in the spinor representation. Eq. (21) is derived from the following Anomalous Green's function[16]

$$F(\mathbf{r},\mathbf{r}',\omega) = \int \Delta(\mathbf{l})G^{\uparrow}_{\omega}(\mathbf{r},\mathbf{l})G^{\downarrow}_{-\omega}(\mathbf{r}',\mathbf{l})d\mathbf{l}. \tag{24}$$

However, Eq. (24) does not satisfy the homogeneity condition after averaging out the impurity positions, that is,

$$\overline{F(\mathbf{r},\mathbf{r}',\omega)}^{imp} \neq \overline{F(\mathbf{r}-\mathbf{r}',\omega)}^{imp}. \tag{25}$$

Substituting Eqs. (22) and (23) into Eq. (24) we find extra pairing terms such as

$$\begin{aligned}\overline{\psi_{\vec{k}\uparrow}(\mathbf{r})\psi_{\vec{k}'\downarrow}(\mathbf{r}')}^{imp} &= e^{i(\vec{k}\cdot\mathbf{r}+\vec{k}'\cdot\mathbf{r}')}[1+O(J^2)+\cdots] \\ &\neq f(\mathbf{r}-\mathbf{r}'). \end{aligned} \tag{26}$$

Even if we assume the (incorrect) constant pair potential, we can not eliminate the extra pairing between $\psi_{\vec{k}\uparrow}$ and $\psi_{\vec{k}'\downarrow}$ because up spin and down spin electrons feel different potentials. Notice that

$$\int \psi^*_{\vec{k}\uparrow}(\mathbf{l})\psi_{\vec{k}'\downarrow}(\mathbf{l})d\mathbf{l} \neq \delta_{\vec{k}\vec{k}'}. \tag{27}$$

In fact, the inclusion of the extra pairing has been claimed the origin of the so-called pair-breaking of the magnetic impurities.[15,17] However the extra pairing terms violate the physical constraint of the Anomalous Green's function.

The remedy is to incorporate the pairing constraint derived from the Anomalous Green's function into the self-consistency equation. The revised self-consistency equation is

$$\Delta(\mathbf{r}) = VT\sum_{\omega}\int \Delta(\mathbf{l})\{G^{\uparrow}_{\omega}(\mathbf{r},\mathbf{l})G^{\downarrow}_{-\omega}(\mathbf{r},\mathbf{l})\}^{\mathrm{P}}d\mathbf{l}, \tag{28}$$

where superscript P denotes the pairing constraint which dictates pairing between $\psi_{\vec{k}\uparrow}$ and $\psi_{-\vec{k}\downarrow}$. Notice that Eq. (28) is nothing but another form of the BCS gap equation,

$$\Delta_{\vec{k}} = \sum_{\vec{k}'} V_{\vec{k}\vec{k}'}\frac{\Delta_{\vec{k}'}}{2\epsilon_{\vec{k}'}}tanh(\frac{\epsilon_{\vec{k}'}}{2T}), \tag{29}$$

where

$$\Delta_{\vec{k}} = \int \psi^*_{\vec{k}\uparrow}(\mathbf{r})\psi^*_{-\vec{k}\downarrow}(\mathbf{r})\Delta(\mathbf{r})d\mathbf{r}, \tag{30}$$

and

$$V_{\vec{k}\vec{k}'} = V\int \psi^*_{\vec{k}'\uparrow}(\mathbf{r})\psi^*_{-\vec{k}'\downarrow}(\mathbf{r})\psi_{-\vec{k}\downarrow}(\mathbf{r})\psi_{\vec{k}\uparrow}(\mathbf{r})d\mathbf{r}. \tag{31}$$

5. CONCLUSION

Using the theory by Kim and Overhauser, we have studied the compensation of magnetic impurity effect in superconductors as a consequence of radiation damage. Good agreement with the experimental data was found. We also showed that Gor'kov's formalism with pairing constraint derived from the Anomalous Green's function gives rise to the KO theory.

Acknowledgments

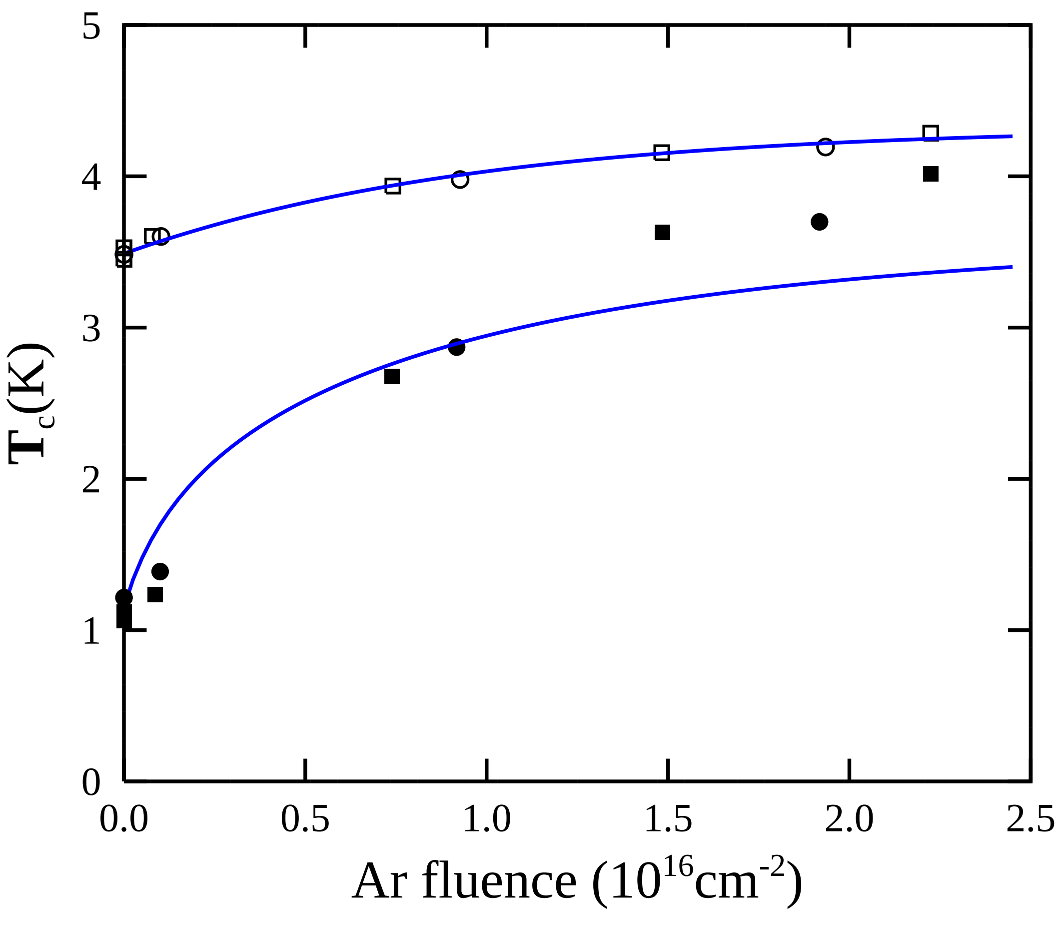
This work was supported by the Korea Research Foundation through Domestic Postdoctoral program. YJK is grateful to A. W. Overhauser for discussions. YJK also acknowledges the supports by the Brainpool project of KOSEF and the MOST.

References

1. Y.-J. Kim and A. W. Overhauser, Phys. Rev. B**49**, 15779 (1994).
2. A. A. Abrikosov and L. P. Gor'kov, Sov. Phys. JETP **12**, 1243 (1961).
3. M. F. Merriam, S. H. Liu, and D. P. Seraphim, Phys. Rev. **136**, A17 (1964).
4. G. Boato, M. Bugo, and C. Rizzuto, Phys. Rev. **148**, 353 (1966).
5. G. Boato and C. Rizzuto, (to be published), (referenced in A. J. Heeger, (1969), in Solid State Physics **23**, eds. F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press, New York), p. 409)
6. W. Bauriedl and G. Heim, Z. Phys. B**26**, 29 (1977)
7. M. Hitzfeld and G. Heim, Sol. Stat. Comm. **29**, 93 (1979).
8. A. Hofmann, W. Bauriedl, and P. Ziemann, Z. Phys. B**46**, 117 (1982).
9. Y.-J. Kim, Mod. Phys. Lett. B **10**, 555 (1996).
10. Y.-J. Kim, Int. J. Mod. Phys. B **11**, 1751 (1997).
11. P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
12. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
13. P. W. Andrson and P. Morel, Phys. Rev. **123**, 1911 (1961).
14. A. Hofmann, P. Ziemann, and W. Buckel, Nucl. Instrum. Methods **182/183**, 943 (1981).
15. P. G. de Gennes and G. Sarma, J. Appl. Phys. **34**, 1380 (1963)
16. A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood, NJ, 1963), Eq. (38.3).
17. P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966) P. 266.

Figure Caption

Fig. 1. Superconducting transition temperature T_c of In (open symbols) and In-Mn (closed symbols) vs Ar fluence. Data are due to Hofmann, Bauriedl, and Ziemann, Ref. 8. $1/\tau_s$ was adjusted in the theoretical curve (lower curve) so that $T_{co} = 1.15K$ without irradiation.



T_c(K)
0
1
2
3
4
5
0.0
0.5
1.0
1.5
2.0
2.5
Ar fluence (10^{16}cm^{-2})